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3,692,525

ULTRAVIOLET PROTECTION OF PHOTOGRAPHIC MATERIALS

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No Drawing. Continuation of application Ser. No. 676,731, Oct. 20, 1967. This application May 14, 1971, Ser. No. 143,619

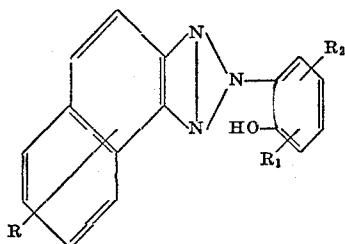
Int. Cl. G03c 1/84

U.S. Cl. 96-84 R

8 Claims

ABSTRACT OF THE DISCLOSURE

A finished photographic element, having a support and, thereon a plurality of developed and fixed photographic emulsion layers containing developed dye images at least one of said dye images being subject to fading by the action of ultraviolet radiation, the emulsion layer containing the developed dye images subject to fading lying between the support and a gelatin layer containing an ultraviolet absorbing hydrophobic compound represented by the following formula:



wherein R, R₁ and R₂ can be hydrogen or an alkyl group of 1 to 20 carbon atoms with at least one of the groups having at least 3 carbon atoms.

This is a continuation of application Ser. No. 676,731, filed Oct. 20, 1967, now abandoned.

This invention relates to a photographic element, and the preparatory process therefor, containing a light-sensitive silver halide emulsion stabilized against the deleterious effects of ultraviolet radiation and, more particularly, to said element stabilized by the incorporation therein of certain naphthotriazoles.

Photographic layers and, in particular, color photographic elements as a result of their sensitization to radiation of longer wave length, are adversely effected by ultraviolet radiation. This deleterious effect also occurs with developed color negatives and prints as a result of the attack on certain chemical species often present in the emulsion layer after development.

Many and varied compounds have been used as ultraviolet absorbers. Criteria for acceptable absorbers include non-diffusibility, freedom from color, inertness, compatibility and, of course, good ultraviolet absorption and stability to ultraviolet. Such compounds have been used either incorporated into the silver halide emulsion layer or in a layer superior but contiguous thereto. Among the methods for accomplishing such incorporation is a solvent-dispersion technique in which the ultraviolet absorber compound is dissolved in an organic plasticizer which is, in turn, intimately blended into an aque-

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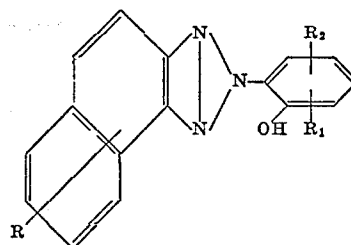
ous gelatin solution. This procedure, however, has certain shortcomings, chief among which is a decrease in the light stability of the incorporated absorber compounds.

It is an object of this invention, therefore to provide compounds affording suitable ultraviolet absorption.

It is a further object of this invention to provide such compounds capable of incorporation into the various components or layers of light-sensitive photographic elements without any loss in their absorption capacity.

In accordance with this invention it has been found that certain naphthotriazole compounds and, in particular, certain hydroxy substituted phenyl naphthotriazoles have superior ultraviolet absorption capacity which is not mitigated by incorporation into emulsions.

Therefore, this invention is based at least in part on the discovery that naphthotriazole compounds having the structure as set forth in the general formula:

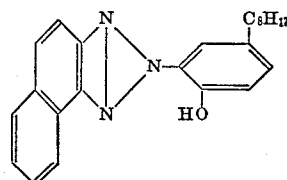


not only have higher ultraviolet extinction coefficients than compounds previously used for this purpose but also provide ultraviolet protection equal or superior to the aforesaid compounds.

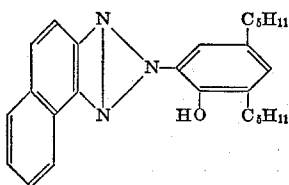
In the above structure, R, R₁ and R₂ each preferably represents hydrogen or an alkyl of 1 to 20 carbon atoms, at least one of the groups R, R₁ and R₂ containing at least mism of less than 250 A. may also be present. These in-said groups being 3 to 24 and preferably being 4 to 16. Other non-chromophoric substituents with a bathochromism of less than 250A. may also be present. These include halogen, preferably chlorine, carboxy, carbalkoxy, cyan, sulfamyl (sulfonamide), carbanyl (carboxamido), etc. Substituted alkyls may also be used as, for example, hydroalkyl, haloalkyl, cyanalkyl, alkoxyalkyl and lactam methylene. Details as to specific substituents can be found in the co-pending application of Catino and Strobel, Ser. No. 504,206, filed Oct. 23, 1965, now abandoned, and in corresponding French Pat. 1,497,191 issued Aug. 28, 1967.

The general method of preparation of these compounds involved the diazotizing and coupling of an orthoamino phenol to an amino naphthalene or the diazotizing and coupling of an o-nitronaphthylamine to a substituted phenol in such a manner that the coupling is either ortho to the amino group of the naphtho ring or ortho to the hydroxy group of the phenol. Details as to this preparatory procedure can be found in the aforesaid U.S. application of Catino and Strobel and the corresponding French patent.

The preferred compositions of this invention include:
2 - (2'-hydroxy-5'-t-octylphenyl) naphtho(1,2-d)triazole,

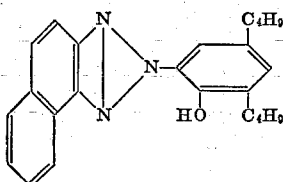


2 - (2' - hydroxy-5'-ditertiaryamyl phenyl)naphtho(1,2-d) triazole,

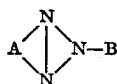


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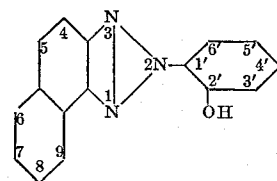
2 - (2' - hydroxy-3',5'-ditertiarybutylphenyl)naphtho(1,2-d) triazole



Characterizing the hydroxyphenyl naphthotriazoles by the general formula:



wherein A represents a naphthalene ring bound by 2 adjacent carbon atoms to two nitrogen atoms of the triazole ring and B represents the phenyl radical containing a hydroxyl group ortho to the nitrogen atom of the triazole ring to which the phenyl radical is linked, the columns below list other substituents suitable for the compositions of this invention.



A	B
Naphtho.....	(2'-hydroxy-5'-N,N-diethylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-methyl)phenyl.
Do.....	(2'-hydroxy-5'-N-morpholinosulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N-phenylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N-benzylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N-piperidinosulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N-n-propylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N,N-diisopropylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-N,N-hydroxyethylsulfamyl)phenyl.
Do.....	(2'-hydroxy-3',5'-dimethyl)phenyl.
Do.....	(2'-hydroxy-3',5'-carbethoxy)phenyl.
Do.....	(2'-hydroxy-3',5'-dichloro)phenyl.
Do.....	(2'-hydroxy-5'-N-methylsulfamyl)phenyl.
Do.....	(2'-hydroxy-5'-cyano)phenyl.
Do.....	(2'-hydroxy-5'-carbonyl)phenyl.
Do.....	(2'-hydroxy-5'-ethylsulfonoyl)phenyl.
Do.....	(2'-hydroxy-5'-N,N-dimethylcarbamyl)phenyl.
Do.....	(2'-hydroxy-3',5'-diethyl)phenyl.
Do.....	(2'-hydroxy-4',6'-dipropylsulfamyl)phenyl.
Do.....	(2'-hydroxy-4',6'-dibromo)phenyl.
Do.....	(2'-hydroxy-4'-methyl)phenyl.
Do.....	(2'-hydroxy-3',5'-dimethyl)phenyl.
Do.....	(2'-hydroxy-3',5'-chloro-5'-bromo)phenyl.
5-methyl naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
5-N,N-dimethylsulfamyl naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
6-N,N-dimethylsulfamyl naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
5-cyano naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
5-methoxy naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
5-acetamido naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
5-carbomethoxy naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
6-isopropoxy naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
6-sulfamyl naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
4-sulfamyl naphtho.....	(2'-hydroxy-3',5'-ditertiaryamyl)phenyl.
Naphtho.....	(2'-hydroxy-3'-N-methylene pyrrolidone)phenyl.

TABLE—Continued

A	B
5	Naphtho..... (2'-hydroxy-3'-N-methylene[2-methyl-5-pyrrolidone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[δ-valerolactam])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[ε-caprolactam])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[β-methyl-ε-caprolactam])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[2-propyl piperidone-6])phenyl.
10	Do..... (2'-hydroxy-3'-N-methylene[2-imidazolidinone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[4-methyl-2-imidazolidinone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[1-cyclohexyl-2-imidazolidinone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[3-morpholinone])phenyl.
15	Do..... (2'-hydroxy-3'-N-methylene[2-butyl-3-morpholinone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[2-thiazolidinone])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[succinimide])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[2,2-dimethylsuccinimide])phenyl.
20	Do..... (2'-hydroxy-3'-N-methylene glutarimide)phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[2-cyanoglutarimide])phenyl.
Do.....	(2'-hydroxy-3'-N-methylene adipimide)phenyl.
Do.....	(2'-hydroxy-3'-N-methylene[2,2-diphenyladipimide])phenyl.
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The compounds are incorporated into the emulsion layer or into a layer contiguous therewith by the solvent dispersion procedure as discussed previously. A representative system uses high-boiling, water-immiscible organic plasticizers. The plasticizer system containing the ultraviolet absorber, and such additives as desired or required, is dispersed in an aqueous gelatin solution with the aid of an emulsifier to produce a finely divided, non-crystalline form of a non-diffusible ultraviolet absorber.

Satisfactory results are obtained when these absorber compounds are used in the concentration range of 20 to 150 milligrams per square foot of applied gelatin layer with the preferred concentration range being 25 to 65 milligrams per square foot where the lower value is preferred for the intimately admixed gelatin-absorber-color former layer and the upper value is preferred for the gelatin-absorber layer superposed on the photographic element to be protected. The actual concentration of ultraviolet absorber is dependent, of course, on the specific chemical compound to be protected and the severity of the ultraviolet exposure of said compound. Color formers, as described in U.S. Pat. 3,092,495, are compounds capable of yielding, upon reaction with the oxidation products of a primary amino development agent, a dye image in a color complementary to the sensitivity of the layer in which it was incorporated.

Several examples are set forth below to illustrate the nature of the invention and the manner of carrying it out. However, the invention should not be considered as being limited to the details thereof.

EXAMPLES 1-7

These examples illustrate the beneficial effects of naphthotriazoles when incorporated in a gelatin layer and used as a superposed ultraviolet absorber layer for developed color film strips.

2.0 grams of an ultraviolet absorber were dissolved in 3 ml. of an equivolume mixture of dibutyl phthalate and butylbenzyl phthalate heated to 100–110° C. This solution was then dispersed in 16 ml. of a 10% gelatin solution and 2.5 ml. of a 10% solution of a propylated naphthalene sulfonate (Alkanol B) by homogenization for 3 minutes with a high speed mixer. The dispersion was then chilled and noodled.

The gelatin layers were prepared by adding 15 grams of the above absorber dispersion (containing 1.2 grams of the ultraviolet absorber) to 200 ml. of a 2.5% gelatin solution containing 5 ml. of saponin and applying this solution to a clear film support such that the dry coating thickness was 4 to 5 microns. These clear gelatin layers were

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processed through the solutions normally employed in color print work.

Sections 1" x 1/2" were cut from the clear film and superposed on the unexposed color print paper which had been processed in the normal manner. These absorber covered strips were then exposed for ten hours in an Atlas Fade-Ometer to the radiation of a single enclosed violet carbon arc in which 20.3% of the emitted radiation is in

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hours in the Atlas Fade-Ometer and subjected to the ultraviolet radiation as heretofore explained. The yellow discoloration resulting from ultraviolet degradation of unused color former was again determined by reflection density measurements. In addition the loss in yellow dye density was determined by similar yellow dye density measurements with correction made for the yellow stain developed. Results are tabulated below.

TABLE II

Ex.	Ultraviolet absorber	UV absorber concentration, mgm./ft. ²	Stain, percent incr.	Yellow dye density, percent loss
8.....	2-(2'-hydroxy-5'-t-octylphenyl)naphthotriazole.	27.5	67	18
9.....	2-(2'-hydroxy-3',5'-ditertiaryamylphenyl)naphthotriazole.	27.5	50	7.5
10.....	2-(2'-hydroxy-5'-t-octylphenyl)naphthotriazole.	54	33	9.6
11.....	2-(2'-hydroxy-3',5'-ditertiaryamylphenyl)benzotriazole.	27.5	100	20.7
12.....	2,2'-dihydroxy-4'-octoxybenzophenone.....	27.5	100	11.4
13.....	do	54	83	7.4
14.....	Blank		260	51.0

the ultraviolet range. For comparison purposes both a blank sample and samples covered with gelatin layers containing ultraviolet absorbers of the prior art were also prepared and exposed.

After this exposure the samples were placed in a densitometer to determine the degree of yellow stain discoloration by reflection density measurements. This discoloration is a result of degradation, by the incident ultraviolet radiation, of the unused color formers remaining in the paper after processing. Results are tabulated below.

TABLE I

Ex.	Ultraviolet absorber	UV absorber concentration mgm./ft. ²	Discoloration, percent incr.	Reflection density reading	
				Initial	Final
1.....	2-(2'-hydroxy-3',5'-ditertiaryamylphenyl)naphthotriazole.	70	25	.12	.15
2.....	2-(2'-hydroxy-3',5'-ditertiarybutylphenyl)naphthotriazole.	70	25	.12	.15
3.....	2-(2'-hydroxy-5'-t-octylphenyl)naphthotriazole.	70	58	.12	.19
4.....	do	35	75	.12	.21
5.....	2,2'-dihydroxy-4'-octoxybenzophenone.	70	25	.12	.15
6.....	2-(2'-hydroxy-3',5'-ditertiaryamylphenyl)benzotriazole.	70	34	.12	.16
7.....	Blank		208	.12	.37

EXAMPLES 8-14

These examples illustrate the suitability of the ultraviolet absorber compounds of this invention when incorporated into one of the color forming layers of a multilayer color photographic element.

Dispersions containing the ultraviolet absorber compound with a cyan color former were prepared following a procedure analogous to that described in Examples 1-7 above with both the ultraviolet absorber and the cyan color former dissolved in the solvents. The dispersion composition was constituted as listed below.

Ultraviolet absorber	grams.....	6.0
Cyan color former - [2,4 - dichloro - 3 - methyl-6(2',4' - ditertiaryamyl phenoxyacetamido)phenol]	grams.....	6.0
Dibutylphthalate	ml.....	6.0
Butylbenzylphthalate	ml.....	6.0
Gelatin	grams.....	6.0
Water	ml.....	60.0
10% Alkanol B (propylated naphthalene sulfonate)	ml.....	10.0

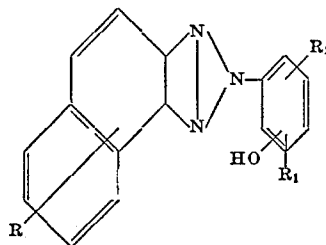
Each dispersion was, in turn, admixed with red sensitized silver halide emulsions containing the necessary coating finals and this mixture was then coated over the yellow and magenta dye-forming layers on a paper support to form a multilayer color photographic element. After the element was given red, green and blue separation exposure and processed, it was then positioned for 10

results are measures of the intra-layer and extra-layer ultraviolet degradation effects respectively, they are indicative of the protective ability of the naphthotriazoles when either intimately admixed in the emulsion layer or applied as an exterior coating over the emulsion layer.

While exemplary embodiments of the invention have been described, the true scope of the invention is to be determined from the following claims.

We claim:

1. A photographic element comprising a support having thereon at least one photographic silver halide emulsion layer and a superposed gelatin layer, at least one of said layers containing a hydrophobic compound having the formula:



wherein R, R₁ and R₂ each represents a member selected from the class consisting of hydrogen, halogen, alkyl groups having from 1 to 20 carbon atoms, hydroxyalkyl, haloalkyl, cyanoalkyl, alkoxyalkyl, alkoxy, aryloxy, cyano, carbalkoxy, alkyl sulfonyl, sulfamyl, N-alkyl sulfam-

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yl, N-phenyl sulfamyl, N-heterocyclic sulfamyl, carbamyl, N-alkyl carbamyl, N-phenyl carbamyl, N-heterocyclic carbamyl and lactam methylene groups, at least one of the groups R, R₁ and R₂ containing at least 3 carbon atoms.

2. A photographic element as defined in claim 1 wherein at least one of said photographic silver halide emulsion layers contains said compound.

3. A photographic element as defined in claim 2 wherein the layer containing said compound is formed from a dispersion comprising a hydrophilic colloid binder material, a high-boiling, water immiscible organic plasticizer and said compound.

4. A photographic element as defined in claim 1 wherein said superposed gelatin layer contains said compound.

5. A photographic element as defined in claim 4 wherein the superposed gelatin layer containing said compound is formed from a dispersion comprising gelatin, a high-boiling water immiscible organic plasticizer and said compound.

6. A photographic element according to claim 1 in

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which the hydrophobic compound is 2-(2'-hydroxy-5'-t-octylphenyl)naphtho(1,2-d)triazole.

7. A photographic element according to claim 1 in which the hydrophobic compound is 2-(2'-hydroxy-3',5'-ditertiaryamylphenyl)naphtho(1,2-d)triazole.

8. A photographic element according to claim 1 in which the hydrophobic compound is 2-(2'-hydroxy-3',5'-ditertiarybutylphenyl)naphtho(1,2-d)triazole.

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UNITED STATES PATENTS

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

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